

THE USE OF SPECIES FORMED BY HIGH TEMPERATURE  
EVAPORATION IN CHEMICAL SYNTHESIS

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Over the last thirty years, there has been growing interest in the high temperature, vacuum evaporation of many solid elements and compounds to form thin films, special alloys and new solid phases. As a result, methods and apparatus now exist for the evaporation of at least a gram an hour of most materials at any temperature up to 3500°C at pressures of  $10^{-6}$  torr or lower.

There has also been increasing study of vapor species formed when materials vaporize at above 1000°C. The species have mostly been identified by their mass spectra or ultra-violet spectra, and vapor equilibrium measurements have been made.

Atoms of the metals and metalloids, vapors of low valent compounds, and vapors of some normal valent compounds, formed at high temperatures, are all "high energy" species. They may be capable of chemical reactions not shown by the original material in the condensed phase at lower temperatures. Yet despite their physical characterisation and commonplace generation for other purposes, the possible use of high temperature vapors as reagents in chemical synthesis has been overlooked until the last few years.

The purpose of this paper is to discuss the conditions necessary to use high temperature species in synthesis, to indicate the synthetic potentialities of such species, and to summarise the results of relevant research underway in the author's laboratory.

Conditions for using high temperature vapors in synthesis

Whenever a vapor is formed by heating a material in the condensed phase, the energy supplied overcomes the forces which hold the

molecules or atoms together. Relative to the condensed phase of the material at room temperature, the vapor is a species of higher energy. For a material with a normal boiling point of above  $1500^{\circ}\text{C}$ , the difference in free energy between the solid at room temperature and its vapor at room temperature will usually be above 30 Kcals per mole. The vapors of metals, with a few exceptions, will be atomic species with free energies of formation of +30 to +180 Kcals relative to the solid metal. Such atomic species may have a chemical reactivity far greater than that of the original metals.

Of course, the vapors formed by evaporation at high temperatures are not stable at ordinary temperatures and will immediately condense to reform the starting material. They can thus be made to undergo gas-phase reactions only with the relatively few other molecules which are stable at high temperatures. However, the potential reactivity of the high temperature vapors towards a wide range of compounds can be exploited by cocondensing the high temperature vapor and the vapor of another compound on a surface at  $-196^{\circ}$ . This requires that the high temperature vapor is generated under high vacuum and passes by a collision free path to a cold surface, on to which another molecule is also being condensed. The high temperature species will either react with itself on the cold surface or with the other molecule. Which reaction is favored depends on both thermodynamic and kinetic factors. Only reactions with an activation energy less than about 5 Kcals can occur to a measureable extent at  $-196^{\circ}$ , but fortunately the reactions of many high temperature species do have very low activation energies.

### Synthetic possibilities of high temperature species

Two types of uses are seen for cocondensation reactions of high temperature species with ordinary molecules at low temperatures. In the first, the high temperature atom or molecule will become incorporated in another molecule with which it reacts. This use has been well illustrated by published work on carbon and silicon vapor, and by reactions of other high temperature species such as boron monofluoride, silicon difluoride, and silicon dichloride<sup>1</sup>. It is to be expected that atoms and homonuclear molecules of almost all metals and metalloids, and molecules like  $BC_2$ ,  $SiC$ ,  $SiO$ , etc., will all react with other molecules to form new compounds which contain the species.

In the second use, the high temperature species may be used as powerful and selective reagents for removal of halogens and other active atoms from molecules. Although nearly all metals might serve in this role, it is to be expected that the greatest selectivity will be shown by the later transition metals, for which intermediates may be governed by particular complexing ability.

### Present work in the author's laboratory

#### A. Methods of Evaporation

Two main methods are being used to evaporated metals and other materials inside a chamber with liquid nitrogen cooled walls, at a pressure less than  $10^{-6}$  torr.

The first is electron bombardment heating using a Varian "e-Gun", which permits downward evaporation from a rod of material. For those materials which melt before evaporation, a molten drop is held on the end of

the rod by surface tension. The rod can be advanced as material vaporises from the tip. The method gives a rate of evaporation of about one gram an hour for most metals boiling below  $3000^{\circ}\text{C}$ , and for carbon, silicon, and boron. The method has the disadvantage that it does not allow evaporation of very large quantities of metals. There is also some uncertainty about the temperature at which evaporation is occurring, and the electronic state of the vapor species formed. Occasionally there have been problems due to stray electrons inside the vacuum chamber exciting the vapor which is being cocondensed with the high temperature species.

The second method is simple evaporation from resistively heated molybdenum boats or baskets, with or without alumina linings. It is easy to evaporate 1 to 3 g. an hour of metals like copper or silver, and it will probably prove the best method for most metals boiling below  $3000^{\circ}\text{C}$ . It can be scaled up to permit evaporation of many grams of a metal.

#### B. Reactions of atoms being studied

##### Boron Atoms

The reactions of boron with hydrogen halides, boron trichloride, phosphorus trichloride, and some organic compounds have already been reported by the author<sup>2</sup>. Further reactions being carried out all tend to confirm the idea that boron atoms react destructively with most compounds. Free radical polymerisation occurs, and the yields of products in which boron has undergone simple insertion into a bond or any similar process, are always low.

##### Silicon Atoms

One reaction of silicon atoms, their insertion into the Si-H bond

of trimethylsilane, has already been reported by Skell<sup>3</sup>. In this work, silicon has been reacted with  $B_2F_4$  in an effort to make compounds in the series  $SiF_{4-n}(BF_2)_n$  (the first two members of this series,  $SiF_3BF_2$ , and  $SiF_2(BF_2)_2$ , have resulted from the action of  $SiF_4$  on boron at  $2000^\circ C$ ). The only new volatile material obtained from the cocondensation of  $B_2F_4$  and Si atoms, has been characterised as  $SiF(BF_2)_3$ . This structure was assigned from its mass spectrum,  $^{11}B$  and  $^{19}F$  nmr spectrum, and infrared spectrum. The compound  $Si(BF_2)_4$  was not formed.

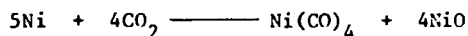
#### Iron Atoms

Iron has been cocondensed with a large excess of benzene in an effort to make the as yet unknown compound dibenzeneiron,  $Fe(C_6H_6)_2$ . On warming the cocondensate to about  $-50^\circ$  under vacuum, most of the benzene could be pumped off. On warming further to  $0^\circ$ , the cocondensate exploded liberating benzene, and a little diphenyl and hydrogen. The residue was metallic iron. If the cocondensate was allowed to warm from  $-50^\circ$  to room temperature in the presence of one atmosphere of hydrogen, there was no explosion. The volatile material which could be pumped off was then mostly cyclohexane. The results suggest that a very unstable iron benzene compound was being formed. The reactivity of benzene in the compound was far higher than usual as it would be reduced to cyclohexane under very mild conditions. The formation of dibenzeneiron would be consistent with the data so far obtained, but more work is necessary to prove its existence.

This work with iron atoms does demonstrate that cocondensation reactions may be a useful route to unstable zero-valent transition metal complexes.

Nickel Atoms

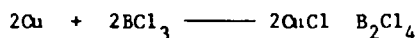
Nickel was cocondensed with carbon dioxide. On warming the cocondensate a little above  $-196^{\circ}$  some carbon monoxide was evolved. About 15% of the nickel deposited was recovered as nickel carbonyl, the rest remained as a black nickel oxide, approximating to NiO in composition. The yield of  $\text{Ni}(\text{CO})_4$  was about 75% of that required by the equation



Nickel was also condensed with boron trifluoride to try to obtain  $\text{Ni}(\text{BF})_4$ . Reaction occurred but the product seemed to be a mixture of a nickel boride and the known complex  $\text{NiF}_2 \cdot \text{BF}_3$ . No evidence of stepwise reduction of the boron trifluoride was obtained.

Copper and Silver Atoms

Copper has been found to be a very effective reagent for removing chlorine from B-Cl bond and coupling the boron atoms. When copper atoms and  $\text{BCl}_3$  were cocondensed in a 1:6 mole ratio,  $\text{B}_2\text{Cl}_4$  was formed in 40% of the yield required by the equation



Using copper atoms and  $\text{CH}_3\text{BCl}_2$ , a similar yield of the new compound 1,2-dimethyl-1,2,-dichlorodiboron was obtained. This was characterised by its mass spectrum and its  $^{11}\text{B}$  and proton nmr spectrum, and by its quantitative reversion to  $\text{CH}_3\text{BCl}_2$  on treatment with chlorine at  $-80^{\circ}$ . The cocondensation reaction of copper with  $(\text{CH}_3)_2\text{BCl}$  was very complex, although an unstable compound  $(\text{CH}_3)_4\text{B}_2$  may have been among the products.

Cocondensation of copper atoms generated by electron bombardment heating with a mixture of  $\text{BCl}_3$  and  $\text{SiCl}_4$ , gave  $\text{B}_2\text{Cl}_4$  and  $\text{SiCl}_3\text{BCl}_2$ . Cocondensation of copper evaporated from a molybdenum boat at  $1400^\circ$  with the same mixture, gave  $\text{B}_2\text{Cl}_4$  but no  $\text{SiCl}_3\text{BCl}_2$ . This is an example of electronic excitation either of the copper vapor or of the  $\text{SiCl}_4$  which can occur with electron bombardment heating.

Silver atoms, formed by evaporation from molybdenum boats, react with B-Cl compounds in a similar way to copper atoms, but the yields are much poorer. The bulk of the silver is recovered as metal from the surface where cocondensation takes place.

References

1. For a general review see P.L. Timms, Endeavour, 27, 133 (1968)
2. P.L. Timms, Chem.Comm., 258 (1968)
3. P.S. Skell and P.W. Owen, J.Am.Chem.Soc., 89, 3933 (1967)